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# IGNITION DYNAMICS IN RELATION TO COMBUSTION DYNAMICS OF DOUBLE BASE PROPELLANTS

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by

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The objective of the research was to elucidate the physical and chemical factors that control ignition of double base propellants. Detailed experimental and analytical investigations were conducted to understand the ignition processes that occur at and near the propellant surface, to determine the connection between the ignitability of a propellant and its other combustion characteristics, to quantify the peculiarities of radiative ignition in comparison

20. Abstract - continued
with hot gas ignition, and to develop a means of ranking propellant ignitability. As a result of these investigations, radiative ignition processes have been explained for a wide variety of propellant and test conditions.

## PREFACE

This research was carried out under Grants DA-ARO-D-31-124-71-G51, DA-ARO-D-31-124-71-G184, DA-ARO-D-31-124-73-G105, DAHCO4 74 G 0124, DAHC04 75 G 0125 from the U.S. Army Research Office in Durham, North Carolina. The technical monitors were Dr. James J. Murray, U.S. Army Research Office and Drs. I. W. May and K. J. White, U.S. Army Ballistic Research Laboratories, Aberdeen Proving Ground, MD.

This report is primarily an administrative document. For the details of the research, the reader is referred to the publications and reports listed on page 2.

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Figure Caption

# IGNITION DYNAMICS IN RELATION TO COMBUSTION DYNAMICS OF DOUBLE BASE PROPELLANTS

## Introduction

The research carried out under the grants was directed at elucidating the physical and chemical factors that control ignition of double base propellants. During the first phase of the research, emphasis was on detailed experimental investigations of the processes that occur at and near the propellant surface, in both the subsurface domain and in the adjacent gas phase domain. During the second phase, studies were conducted to establish the connection between the ignitability of a propellant and its other combustion characteristics. Also, emphasis was placed on quantifying the peculiarities of radiative ignition in comparison with other modes of ignition.

With respect to the connection between the ignitability of a propellant and its other combustion characteristics, the work has shown for double base propellants that appropriate measurements of dynamic combustion phenomena can be employed as a quantitative measure of ignitability. Indeed, this research developed an approach in terms of both theory and apparatus that bypasses the need for difficult to obtain physical and chemical information on the ignition process, and, instead, uses properties that can be measured directly.

The ignition trends of different propellant types (e.g., AP composite vs double base) and of several modified propellants (e.g., noncatalyzed vs catalyzed double base and transparent vs opaque propellants) have been rationalized in terms of basic differences in the structure of the deflagration wave in the solid and gas phases. In addition, for each propellant the data clearly isolate the domains (pressure, ignition stimulus, and propellant type) where simple thermal theories fail and those domains where theories taking into account the interaction of the incipient gas phase with the solid phase are required.

Publications and Reports

The results of our research on solid propellant ignition and related topics were the subjects of technical papers and reports. Since the technical papers were distributed as they became available, this report merely contains the title of the publications.

The publications have been archived by the appropriate agencies. Some types of publications (i.e., progress reports, administrative summary reports and informal presentation summaries) have not been included if the results reported in them are also contained in a more comprehensive archive publication. It should be noted that the interplay among the publications is great since there has been a commonality of propellants, fuels, data reduction techniques, etc. throughout our investigations.

The results of this research have been reported in the following reports and papers:

1. "Temperature Sensitivity of Double-Base Propellants," Proceedings of 8th JANNAF Combustion Meeting, Nov. 1971, CPIA Publication 220, pp. 387-401, N. Kubota, L. H. Caveny and M. Summerfield.
2. "Rate Controlling Processes in Double Base Propellant Ignition," 1st Review of AMC Fundamentals of Ignition Task, Nov. 1971, M. Summerfield, T. J. Ohlemiller, L. H. Caveny, and L. DeLuca.
3. "Sheet-Form Nitrocellulose-Based Propellant Reinforced by Cotton Fabric," Memorandum Report, July, 1972, M. Summerfield and L. H. Caveny.
4. "Dynamic Effects on Ignitability Limits of Solid Propellants Subjected to Radiative Heating," Proceedings of Fourteenth Symposium (International) on Combustion, 1973, pp. 1269-79. T. J. Ohlemiller, L. H. Caveny and M. Summerfield.

5. "Ignition Dynamics of Double Base Propellants," AMS Report No. 1150, January, 1974, Princeton University, M. Summerfield, L. H. Caveny, T. J. Ohlemiller and L. DeLuca.

6. "A Comparative Study of Radiative Ignition Characteristics of Solid Propellants. Part I. Effect of Propellant Formulation," L. DeLuca, L. H. Caveny, T. J. Ohlemiller, and M. Summerfield, to appear in AIAA Journal.

7. "A Comparative Study of Radiative Ignition Characteristics of Solid Propellants. Part II. Pre-Ignition Events and Effects of Radiative Source," L. DeLuca, T. J. Ohlemiller, L. H. Caveny, and M. Summerfield, to appear in AIAA Journal.

8. "Propellant Optical Properties and Ignition Characteristics as Modified by Particulate Carbon," AIAA 13th Aerospace Sciences Meeting, Jan. 1975, Pasadena, Ca., Paper No. 75-231, L. H. Caveny, M. Summerfield and I. W. May, to be submitted for publication.

9. "Ignition and Other Unsteady Combustion Phenomena Induced by Radiation," Ph.D. Thesis in preparation, April 1975, L. DeLuca.

Summary of Research

The several classes of propellants that were examined experimentally include:

Four ammonium perchlorate (AP)/hydrocarbon binder composite propellants:

Nonmetallized -

1. 75% AP (45μ) without C
2. Same as 1 but with 1% C
3. 85% AP (30% 7.5μ & 70% 180μ)

Metallized -

4. 24% AP and 51% boron

Six double base propellants:

5. Standard U.S. Army M-9
6. NC plastisol (53.7% NC, 39.2% MTN, 7.1% TEGDN)
7. Opacified NC plastisol, No. 6 with 0.2% C
8. Opacified NC plastisol, No. 6 with 1.0% C
9. Standard U.S. Navy N-5
10. Catalyzed NC plastisol No. 6 with 2.0% Pb and Cu salts.

Nitramine/Polyurethane (PU) propellants:

11. High energy cool propellant (85% HMX, 15% PU)
12. Fire retarded Propellant (75% HMX, 15% PU, 10% oxamide)

The experimental techniques and measurements included: ignition time versus radiant heat flux and pressure; radiation pulses to induce extinction; highspeed shadowgraphs during the ignition sequency; temperature measurements by means of micro-thermocouples (3μ wire size) placed on the surface and embedded below the surface; IR detection of first flame; and preignition gasification rate versus heat flux and pressure. From these experiments we obtained information concerning the thermal processes leading to stable burning, i.e., heat-up to surface gasification, gasification prior to flame development, flame development, transient burning as the flame is established.

During the first phase of our studies, the data from the experiments were used to establish the following observations concerning the flame structure of double base propellants:

1. At high pressures, the modeling process may be simplified to a condensed phase ignition theory explicitly incorporating only the kinetics and energetics of the surface reactions.
2. At low pressures (and very high fluxes at high pressures) the above simplification is not possible since flame reactions are important for the development to the point of stable ignition; under these conditions, the model must incorporate a description of the kinetics and energetics of the full foam and fizz zone reactions.
3. The effect of platonizing catalysts on ignition behavior is considerable -- dynamic extinguishment effects are eliminated and stable ignition at low pressure becomes possible. These effects of such catalysts appear largely due to acceleration of gas phase reactions above the ignition surface. The strong effects imply a need to ascertain the nature of the new kinetic pathways in platonized propellants if their ignition behavior is to be understood completely.
4. Radiation-assisted burning studies provide a means for obtaining absolute values for the important surface and gaseous feedback energetic terms (and their variation with composition) when supplemented with temperature sensitivity and thermocouple survey studies. The results from these studies tend to confirm that the major effect of platonizing catalysts is acceleration of gas phase reactions near the propellant surface; an ultraviolet photochemical mechanism does not appear to be involved.

Many of the observed ignition processes were explained by the mathematical model which is an extension of the approach

taken by Zeldovich. The significance of these studies goes beyond an explanation of observed ignition and extinguishment limits. By developing the capability of correlating the trends observed in the relatively uncomplicated go/no-go ignition test, the analytical method simultaneously qualifies as being suitable for considering more complex practical situations that involve nonuniform heating, transient pressure fields, complex geometries, etc.

During the second phase of the flame structure studies an understanding of four effects that seriously alter relative ignitability of different propellant classes were developed:

1. Radiation penetration (even slight) lengthens ignition time significantly; opacity becomes an important factor.
2. Cool gas boundary layer in arc-image test (as against hot layer of rocket or gun conditions) lengthens ignition time also.
3. For some propellants (notably NC types but not AP types), the boundary between go and no-go is strongly affected by rate of de-radiation (i.e., shutter closing time).
4. Boundary between go and no-go domains is sensitive to particular intensity profile of "focal footprint" of the beam striking the propellant surface.

These four peculiarities of arc-image and laser ignition make it very difficult to equate radiative ignition with practical ignition situations. However, the peculiarities were used to bring out different flame characteristics of propellants.

The ignition and transient combustion of NC propellants, HMX crystals, and AP crystals were studied using results from high speed (5000 frames/sec) shadowgraphs and color movies. The ignition source was the laser. The tests were carried out in $N_2$ and $CH_4$. A $CH_4$ atmosphere was used in an effort to promote gas phase reactions between the decomposition vapors (e.g., HMX and AP) and the surrounding gases. The three systems differ greatly: (1) the AP monopropellant flame is relatively

cool (1200-1400 K) and close to the surface; (2) HMX burns as a monopropellant with a very hot flame (> 3000 K) that is very nearly balanced but relatively slow to develop; and (3) NC burns with a moderately hot flame that extends several mm from the surface. Furthermore, the films indicated that HMX crystals fracture during rapid ignition. This fracture is important evidence that supports the theory that thermal stresses contribute to the exponent shift of HMX composite propellants. The nearly parallel plumes from AP surface support the theory that AP gas phase reactions are completed at the surface. Expansion of gas above the HMX crystal indicates that a large portion of the HMX gas phase reactions occur above the surface.

Studies were conducted that related measured reflection and absorption properties to the measured ignition characteristics of a series of double base propellants. The measured reflectivities and absorptivities confirm that propellants generally absorb most of the 10.6μ radiation from the $CO_2$ laser within a small fraction of the thermal wave thickness. Thus the propellant optical properties are of secondary importance when considering the thermal effects of $CO_2$ laser radiation on burning and ignition. However, the reflectivities and absorptivities in the 0.4 to 1.6μ range of the xenon arc-image source prominently affect the heat-up to ignition process. Furthermore, since the optical properties are very wave-length dependent and are altered greatly by small percentages of particulate carbon and by residue on burning surfaces, interpreting arc image data is a tedious and imprecise process. The optical property data summarized in the paper on the subject provide guidelines for determining how reflectivity and absorptivity should be treated. Future radiative ignition models can be tested against the consistent sets of optical property data and ignition maps. An important area of future application

of the model and the optical property data is in the analysis of the observed reduction in rocket motor combustion instability attributed to adding carbon powder to nonmetallized propellants.

Characterization of Ignition Events

As a means of efficiently presenting and interpreting the experimental results, we chose to describe the ignition events and limits in terms of the ignition map shown in Fig. 1. Figure 1 shows a traverse of event limits (or signals) on an ignition map. The traverse is at a fixed value of pressure and radiant flux intensity. The events traversed on the ignition map are:

- $L_{1a}$ the surface is heated to the point that it is being gasified and a carbonaceous layer may form on the surface but vigorous exothermic reactions are not occurring. For any lesser heating time, no visible effect is seen.
- $L_{1b}$ either gas phase or surface reactions begin to accelerate rapidly (as indicated by the appearance of detectable IR emissions from the gas just above the sample surface).
- $L_{1c}$ incipient flame appears.
- $L_{1d}$ self-sustaining ignition.
- $L_2$ rapid deradiation (of some propellants) between limits $L_2$ and $L_3$ results in dynamic extinguishment.
- $L_3$ sustained combustion following deradiation (assured by flame spreading away from the target area of radiant heating).

Limits $L_{1d}$, $L_2$, and $L_3$ must be established by go/no-go testing.

The limits $L_{1d}$, $L_2$, and $L_3$ are very specific limits whose positions (and even existence) are strongly dependent on propellant type and test conditions (i.e., pressure, atmosphere, deradiation time, spatial distribution of radiant beam, etc.). Furthermore, as indicated on Fig. 1, the limits $L_{1a}$, $L_{1b}$, $L_{1c}$, and $L_{1d}$ may not be detectable as four individual limits since two or more of the limits may occur nearly simultaneously, depending on pressure, heat flux, and atmosphere. When all four limits occur nearly simultaneously, the limits will be referred to simply as the $L_1$ limit.

In terms of limits shown on Fig. 1, the conditions for ignition may be treated as two essential conditions. The first is the development of the initial exothermic reactions, (i.e., limits $L_{1a}$, $L_{1b}$, and $L_{1c}$) partially within the propellant surface reaction layer and partially in the adjacent gas phase boundary layer. Corresponding quantitative theories have evolved to treat this condition: one of the earliest was the theory of Frazer and Hicks[1] which dealt with the condensed phase; detailed physical modeling of the flame has come from Princeton (e.g., Ref. 2 - 4); and there have been other contributions (e.g., Ref. 5 - 10). The second condition is focused on the final stage of the surface reactions and flame development and emphasizes the conditions for flame retention after the heat source is removed, i.e., limit $L_{1d}$. We call this second condition a late-stage type of theory in contrast to the first condition which we call the early-stage type of theory. In the late stage, attention is focused on matching of the heat feedback from a quasi-steady (fully developed) flame to the heating rate required to prepare the condensed phase for burning. There are many instances in which the appearance of visible flame does not insure self-sustaining combustion. The importance of the late stage theories was emphasized in Ref. 11.

Our experimental and theoretical work[11] described the conditions under which a nitrocellulose double base (DB) propellant can be brought successfully to ignition in terms of the late stage definition (self-sustaining combustion following deradiation, i.e., $L_{1d}$ is crossed), but, if the heating time is increased beyond $L_2$, the propellant will fail to retain the flame following rapid deradiation and the propellant stops burning. This dynamic extinction occurs because the heat flux from the flame is too low to maintain the energy required by the condensed phase during the thermal relaxation period immediately following the overdriven situation of radiation assisted burning. To our knowledge to obtain such a dynamic extinguishment, radiant heating following the $L_{1d}$ limit must drive the burning rate above the steady state burning rate.

The upper limit, $L_3$, above which dynamic extinction does not occur, corresponds to the time required for flame to spread over the irradiated surface beyond the target area of direct exposure. Under these conditions, the dynamic extinction (following rapid deradiation) is restricted to the portion of the propellant surface exposed to the radiant beam; the unperturbed deflagration wave surrounding the target area can reignite the entire surface. Since the long exposure times cause the one-dimensionality of the ignition process to break down, the subsequent disappearance of dynamic extinction is referred to on the ignition maps as "3-D reignition".

Measurement of the time to the prescribed level of IR emission from the propellant surface reveals that the appearance of the (incipient) flame corresponds to a well defined boundary, $L_{1c}$. Significantly, the beginning ($L_{1b}$) of the rapidly accelerating infrared (IR) signal from the propellant surface region is independent of pressure and $O_2$ concentration, but whether and how rapidly strong surface reactions occur depend on both. Therefore, the appearance of initial surface reaction ($L_{1b}$ limit) is controlled by condensed phase and surface processes and can be described by simple thermal theory. However, as previously pointed out, neither the appearance of an incipient flame ($L_{1c}$ limit) nor condensed phase thermal theories ($L_{1a}$ or $L_{1b}$ limits) are in general adequate for declaring that sustained ignition (crossing of $L_{1d}$ limit) will occur. In particular situations (e.g., high pressure and low heat flux), the condensed phase thermal profile is well established and the propellant is able to provide vigorous energy feedback to the surface and rapid flame development occurs; the requirements for a self-sustaining flame are automatically satisfied when a prescribed surface temperature is achieved. In this case, no late-stage theory is needed and the ignition is assured by crossing the $L_{1a}$ limit.

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GENERALIZED IGNITION MAP SHOWING EVENT LIMITS

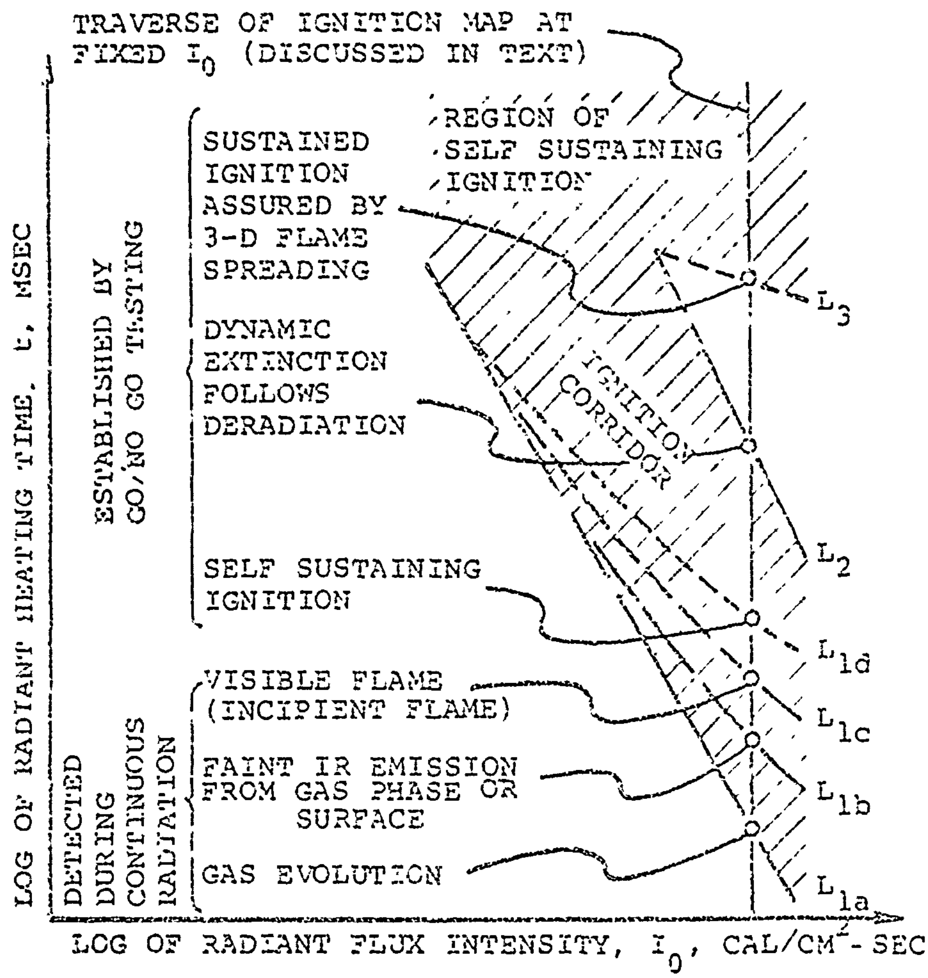


Fig. 1 Generalized ignition map showing event limits or signals that occur during radiant heating of solid propellants.